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A METHOD FOR ULTRA TRACE METAL DETERMINATION IN ACID
PRECIPITATION SAMPLES USING HIGH PERFORMANCE ION CHROMATOGRAPHY
AND INDUCTIVELY COUPLED PLASMA SOURCE MASS SPECTROMETRY

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Environmental scientists studying the affects of acid precipitation on lakes and streams need reliable information on the elemental concentrations in different sample matrices. For example, trace elements such as cadmium and lead can be toxic to aquatic life at concentrations in the nanogram per litre range and may act synergistically with other components of acid rain to further the detriment of the environment (1). Consequently, reliable analytical methods to detect and quantify ultra low-level trace elements are needed to map affected regions and to support studies of toxicity at low concentrations. Few conventional analytical instruments can obtain the detection limits for analytes required in some of these studies. However, instrument performance can be dramatically improved through sample preconcentration.

The conventional method of preconcentration involves quantitative transfer and overnight evaporation. This method is labour intensive, time consuming and can introduce inaccuracies caused by contamination. To minimize these errors, an automated technique has been developed to preconcentrate samples in a closed system using a high performance ion chromatograph (HPIC). A commercially available cation exchange column (2) is used for the preconcentration. The mobile phase is delivered to the column using a high pressure pump and valve system. Depending on the preconcentration factor required, a known volume of sample is deposited on the column. The analytes are then eluted from the column using a relatively strong acid. The preconcentrated "plug" or solution is then introduced into an inductively coupled plasma mass spectrometer (ICP-MS) to determine analyte concentration. The advantage of using an ICP-MS is the high sensitivity and a very fast sequential scanning ability. These capabilities further enhance the preconcentration step to obtain both ultra low detection limits and rapid multielement analysis.

In the method development, optimization of the HPIC to the ICP-MS was necessary to obtain peak performance. Parameters that were investigated were column capacity, variations in concentration and flowrate of two different eluents (nitric and hydrochloric acids), and effects of varying sample pH. The optimum conditions for the above parameters were obtained experimentally. The most favorable settings to produce well defined narrow analyte peak widths were used since the ICP-MS uses peak height measurements for concentration calculations.

Column Capacity. Column capacity was determined experimentally by monitoring the analyte signal of a known standard in the mobile phase as it emerged from the column. Breakthrough was indicated when the continuously monitored signal increased significantly above the background signal. The column capacity was determined to be in the order of 6 micro-equivalents for each element studied.

Effects of Eluent Strength on Retention Time. Experimental results show that the removal of cations from the column is dependent on the acidic strength. In general, the higher the acid concentration of the eluent, the shorter the retention time. A series of experiments were conducted with nitric and hydrochloric acids. Nitric acid at a concentration of 5% was the optimum eluent.

Flowrate. Effects of flowrate on retention time were determined by monitoring elution profiles of analytes while changing the flowrate of the eluent. Experimental results showed that as the flowrate increases, the retention time decreases. The optimum flowrate obtained was 3.5 ml/min.

Effects of Sample pH. Samples submitted to our laboratory may vary in pH, and any analytical method chosen for sample analysis must ensure that variations in sample pH will not bias the accuracy of the results. Experimental results show that varying the pH range of a sample from 1.6 to 9.5 did not adversely affect HPIC-ICP-MS response. Therefore bias in the results will not take place and samples need not be adjusted in this range.

Copper, cadmium and lead were chosen as test analytes because of their significance in many environmental studies. They are also representative of the mass range that is most frequently scanned. The HPIC-ICP-MS detection limits for these elements are in the sub - nanogram per litre range.

During the initial method development stages, the HPIC was interfaced directly with the ICP-MS for ease of experimental study. To preconcentrate a sample to gain reasonable detection limits, a significant volume of sample must be loaded onto the column. If more than one sample is to be analysed, this could be a lengthy procedure. In order to reduce to length of analysis time and to allow the ICP-MS to be used for other tasks, the HPIC has been automated to run "off-line" from the ICP-MS.

The "off-line" HPIC technique has reduced operating cost and freed personnel for other duties. A Zymark robot arm is used to sample from up to 24 sample containers of 100 mL each. The sample is then introduced to the HPIC and the fraction is collected by an ISCO auto-sampler configured as a fraction collector. The Zymark computer controls the robot arm, the switching of the electrically actuated rotary valves in the HPIC system and the sequences for the fraction collector. This automated technique can be run overnight and unattended.

Experimental results show that the method is accurate in the determination of trace metal concentrations in acid precipitation. However, with a different matrix such as surface water and depending on the geographic location of the sample sites, uncertainties in accuracy can be expected with increasing concentration levels of major elements such as Ca and Mg. Investigations in modifications to the chromatographic procedure to reduce these effects will be conducted in the future.

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